IMPROVED SEPARATORS
FOR
SILVER OXIDE-ZINC
AND
SILVER OXIDE-CADMIUM CELLS
FOR SPACECRAFT APPLICATION

by

HELMUTH L. PFLUGER
and
HOWARD E. HOYT

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NOVEMBER 10, 1964 — FEBRUARY 9, 1965

prepared for
GODDARD SPACE FLIGHT CENTER
CONTRACT NAS 5-9107

THE BORDEN CHEMICAL COMPANY
Central Research Laboratory
Philadelphia, Penna. 19124

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PROJECT PERSONNEL

In carrying out the experimental work herein reported, the writers were assisted at The Borden Chemical Company by Dr. Michael Pang, Assistants Ronald G. Burton and Charles J. Guinosso, and Dr. George Kitazawa, Head of the Physical Testing Laboratory. At Burgess Battery Company, the sub-contract tests were under the supervision of Mr. Frederick A. Poss and Mr. J. R. Beckman.

12870

A study has been made of the diffusion of silver oxide through separator membranes, using radioactive silver and an improved technique. Three different types of membrane behavior were found:-

(1) Membranes composed of methyl cellulose intimately mixed with carboxylated polymers (B and C types developed in previous Contract NAS 5-3467) took up only very small amounts of silver but allowed small amounts of silver oxide to diffuse through. Cells with these separators resist short-circuiting.

(2) Membranes composed of cellophane or polyvinyl alcohol, or compositions containing large amounts of hydroxyethyl cellulose reduce considerable amounts of silver oxide to metallic silver, allowing relatively small amounts to pass through. Cells with these membranes show a tendency to short-circuit.

(3) A film of "S-type" polymer developed under another project was unique in that it showed very little tendency to either pick up silver or let it pass through. In its unmodified form, however, it developed high internal resistance in cell tests.

Exploratory experiments on copolymerization of methacrylate esters with acrylic acid indicate advantages in preparing these by hydrolysis of corresponding copolymers of methyl acrylate with methacrylates. A promising quadripolymer was made from methyl methacrylate, isoprene, acrylonitrile and acrylic acid.

Some less common cellulose derivatives were explored. A commercial product called Ethulose deserves further study.

Preliminary investigations were made on ethylene copolymers containing polar groups and on chlorophosphation of several polyolefins. These polymers are of primary interest as being potentially resistant to high temperatures.

I. INTRODUCTION

Under the preceding contract (NAS-5-3467) several types of membrane were developed which had properties superior to cellophane when used as separators in alkaline·silver-zinc cells. In this development, the principle was established that the separator must possess a balance between polar and non-polar structural character. Polarity must be high enough to obtain electrolyte absorption and electrolytic conductivity, but non-polarity must be sufficient to prevent solubility in concentrated alkali.

The most successful application of this principle made under the preceding contract was obtained by combining the moderately polar polymer methyl cellulose (MC) with the highly polar 1:1 copolymer of vinyl methyl ether with maleic anhydride (PVM/MA). In cycle tests run by Burgess Battery Co., cells with such materials went through 35 to 41 cycles before reaching 60% of nominal capacity and suffered no catastrophic failure. By contrast, corresponding cells with cellophane separators shorted after 15 to 21 cycles. Tests subsequently made at Crane Ammunition Depot, to be reported by NASA/GSFC, showed that cells with MC:PVM/MA in the ratio 7:3 went through 85 cycles before reaching 40% of nominal capacity, again with no shorting. Work in the preceding contract showed that this behavior correlates with extremely high stability to oxidation and a negligible rate of silver ion diffusion through the membrane.

In directing the course of the present contract (NAS-5-9107) toward further improvements, three approaches in particular are being taken:

1) The more successful materials of the preceding contract are being studied in greater detail. In particular the rate of silver diffusion through them has been studied.

2) Modification of the methyl cellulose combinations are being investigated with the objective of obtaining higher polarities more suitable for use at 40 and 45 percent potassium hydroxide.

3) Synthesis of new polymers is being undertaken, aiming primarily to achieve the required balance of polarity within the same molecule. During the first quarter, much of the synthetic work was exploratory and covered a wide range of types. In continuing the work, more promising types are being studied in greater depth.

The progress reported in this First Quarterly Report covers work done in the first and third of these approaches.

SECTION A - SILVER DIFFUSION

Procedure:

The radioactive tracer technique used to study diffusion of silver ions has been described in a previous report (1). The apparatus is based on earlier work of Dirkse (2) and Electric Storage Battery Company scientists (3,4) but incorporates improvements which avoid silver losses on the walls of the cell. These improvements consist in the use of pyrex glass instead of polymethacrylate in the half-cells and polyethylene gaskets rather than neoprene.

The diffusion cell is illustrated in Figure 1. The half-cells are standard commercial pyrex glass ells with one-inch internal diameter. These are clamped together with standard aluminum flanges using flat polyethylene gaskets on both sides of the membrane to be tested. The ring-seal Teflon gaskets employed commercially with the ells were found equally resistant to silver oxide but required greater care in handling than polyethylene in order to avoid rupturing the membrane.
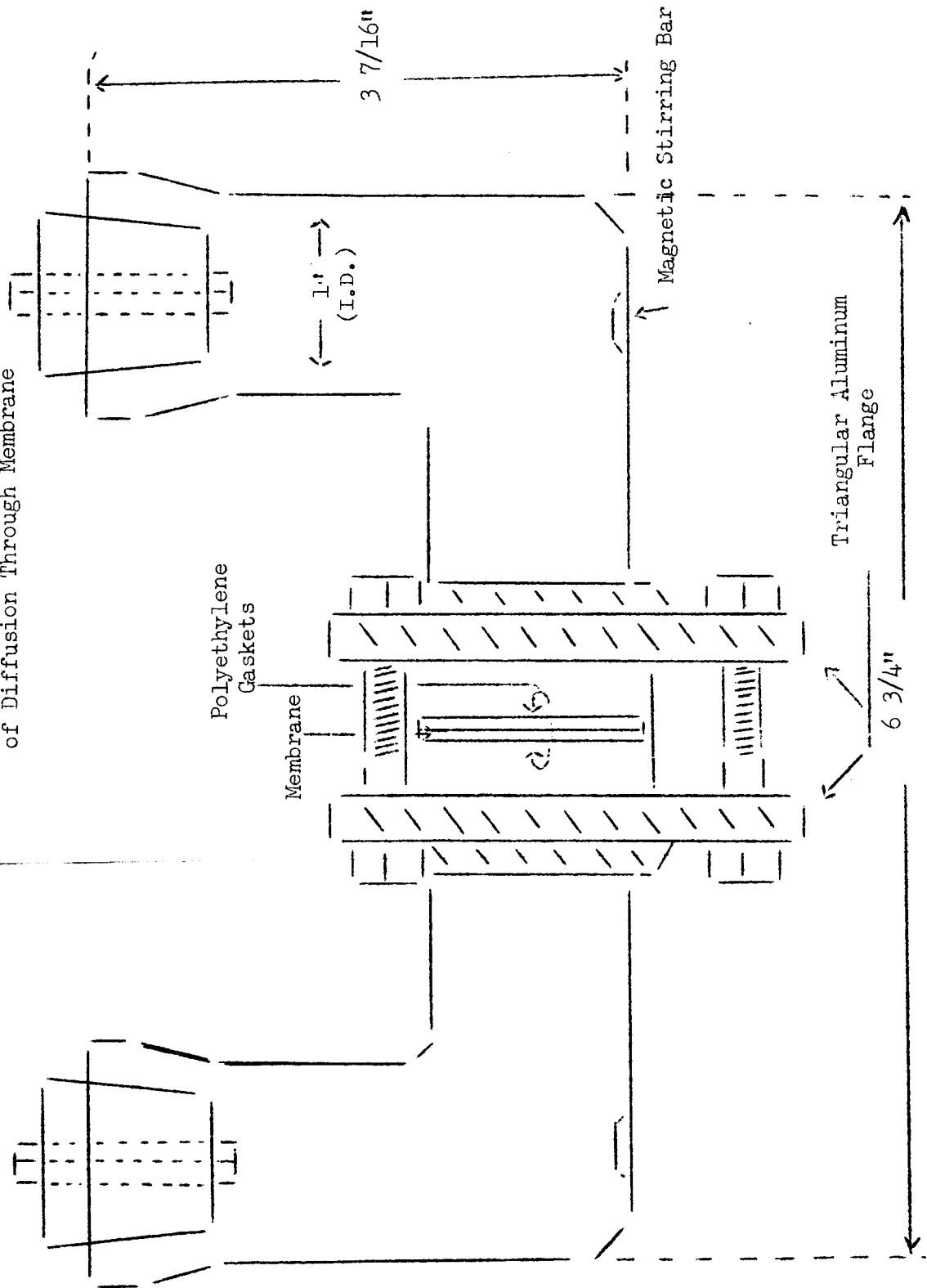
Circular disks of membranes, 1.5 inches in diameter, were cut by means of a punch. Stirring was achieved magnetically with a half-inch Teflon stirring bar on each side. The neoprene stoppers used to close each half were not allowed to come into contact with silver solution and were fitted with capillary tubes to permit equalization of pressure.

The usual precautions were taken against spillage and radioactive contamination. The stand holding the assembled cell was placed in a glass dish under a hood. The laboratory bench was protected with disposable paper.

The radioactive solution was prepared by treating 30% aqueous potassium hydroxide solution with silver nitrate solution enriched with Ag 110 (Oak Ridge). The amount of silver nitrate was just in excess of that necessary to saturate the solution with silver oxide. To ensure saturation, the solution was magnetically stirred in contact with the precipitated silver oxide in the dark overnight.

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(1) H.L.Pfluger and H. E. Hoyt, Final Report Contract NAS 5-3467 June 28, 1963 to November 9, 1964, Appendix II.

(2) T. P. Dirkse, Chapter 10 in "Characteristics of Separators for Alkaline Silver-Oxide-Zinc Secondary Batteries", edited by J.E.Cooper and A. Fleischer, AF Aero Propulsion Lab, Wright-Patterson Air Force Base, Ohio (1964).

(3) E. Weiss, A. J. Salkind and C. G. Oberholzer, Fourth Quarterly Report, Contract NAS-5-2860, March 29 to June 28, 1963.

(4) E. Weiss, J. B. Ockerman and C. G. Oberholzer, Fifth Quarterly Report, Contract NAS-5-2860, June 29 to Sept. 28, 1963.

Figure 1 – Glass Cell for Measurement of Diffusion Through Membrane

Magnetic Stirring Bar

3 7/16"

1" (I.D.)

Triangular Aluminum Flange

Polyethylene Gaskets

Membrane

6 3/4"

The amount of nitrate ion introduced by this procedure was negligible, being of the order of 0.002 mole percent with respect to hydroxide ion. Nevertheless, the non-radioactive stock solution was prepared in a similar way using non-radioactive silver nitrate solution.

After equilibration with the precipitated silver oxide, the stock solutions were filtered into brown storage bottles through sintered glass funnels. The funnels were prepared for this operation by successive treatments with hot nitric acid followed by thorough washing with distilled water and drying.

Each experiment was carried out as follows. The clean and dry cell was assembled with membrane inserted between the two sides. A 45.0 ml. portion of the radioactive stock solution was pipetted into Side 1. Immediately thereafter, a 45.0 ml. portion of the non-radioactive solution was pipetted into Side 2. Periodically, duplicate 0.05 ml. aliquots were pipetted from each side to stainless steel planchets one inch in diameter (Nuclear Chicago Corporation). To assure homogeneity the solutions were magnetically stirred for one minute before sampling. The planchets were dried under an infra-red lamp. Radioactivity was measured with a scaler (Baird-Atomic Instrument Co. Model 1091) and flow counter (Packard Instrument Co., Model 210). Radioactive counts were corrected by subtraction of the "noise count".

Typically, the observed counts/min. changed from more than 400 to about 200 on the initially radioactive side 1. The "noise" count was usually about 30 counts/min. Statistical analysis of a large number of duplicate 0.05 ml. samples indicated the standard deviation for duplication is about ± 10 counts/min. On a percentage basis, this corresponds to a standard error ranging from 2.5% to 5.0% on Side 1 as the radioactivity decreases. On side 2, the error is initially extremely high, becoming lower as radioactivity increases but being not much better than 10% at the termination of the typical experiment.

Since the half-life of Ag 110 is 249 days, its radioactivity is decreased only by about 2% in one week. In the experiments which were carried out within less than one week each, it was therefore possible to ignore the decay of radioactivity as negligible in comparison to the above mentioned experimental errors.

The solubility of silver oxide in 30% KOH at 25° C., as measured by Amlie and Ruetschi (5), is 57 mg per liter. Using this value and the radioactive counts/min. for initial solution and for cell solutions on both sides of the diffusion cell at various times, calculation was made of the respective amounts of silver oxide which remained on the initially radioactive Side 1 and which had diffused through to the opposite Side 2. These are summarized in Table I together with corresponding weights of silver oxide taken up by the membranes.

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(5) R. F. Amlie and P. Reutschi, J. Electrochemical Soc., 108, 813-819 (1961).

Table I

Silver Diffusion Through Membranes
From 30% KOH Solutions Saturated with Ag_2O

Membrane Type (*)	Expt. No.	Time (Hrs.)	Disposition, At End of Experiment of Silver Oxide Originally On Side 1. - In Milligrams Estimated from Radioactivity				Total Silver Oxide Taken Up By Membrane From Both Sides
			Side 1	Side 2	Membrane	Sum	in Milligrams
B3	7	66	2.04	0.39	0.03	2.46	0.065
	14	146	1.49	1.03	.10	2.62	.195
	15	188	1.65	1.21	.13	2.99	.265
C1	6	118	2.16	.37	.23	2.76	.449
C2	18	173	1.56	.80	.17	2.53	.346
C3	8	66	1.71	.39	.14	2.24	.279
	5	161	1.41	.85	.33	2.59	.665
	16	188	1.43	1.14	.23	2.80	.467
PVAlc 79	12	66	.89	.06	1.88	2.83	3.76
PVAlc 374-61	10	92	1.08	.07	1.81	2.96	3.62
E4	11	66	.72	.08	1.76	2.56	3.51
Cellophane	13	146	.62	.11	1.76	2.49	3.54
Copolymer S	9	92	2.03	.11	.08	2.22	0.158
	17	173	1.84	.61	.04	2.49	.079

(*) B3 = 7 parts methyl cellulose, 3 parts polyacrylic acid
   C1 = 9 parts methyl cellulose, 1 part PVM/MA
   C2 = 8 parts methyl cellulose, 2 parts PVM/MA
   C3 = 7 parts methyl cellulose, 3 parts PVM/MA
        where PVM/MA = 1:1 copolymer of vinyl methyl ether and maleic anhydride.
   PVAlc 79 = 8 parts 88% hydrolyzed PVAlc, 2 parts tetraethylene glycol.
   PVAlc 374-61 = Completely hydrolyzed polyvinyl alcohol
   E4 = 6.5 parts methyl cellulose, 3.5 parts hydroxyethyl cellulose
              (Union Carbide QP09).
   Cellophane = PUDO grade
   Copolymer S = proprietary product; see Section C below.

The amount of radioactive silver oxide deposited on the membrane at the end of an experiment was determined from the radioactive count of a solution of the membrane in nitric acid. The membrane was removed from the cell and washed with plain 30% KOH, then padded dry with filter paper. A weighed amount of concentrated nitric acid was used to dissolve the membrane and its contents. A 0.05 ml. aliquot of this solution was transferred to a planchet, evaporated to dryness, and counted. From this and the usual calibration factors, the weight of radioactive silver oxide on the membrane was calculated. Since silver oxide was taken up from both sides of the membrane the total amount was estimated to be roughly twice that indicated by the radioactivity. (This estimate is in error to the extent that some radioactive material which has diffused to Side 2 comes back on to the membrane.) No attempt was made to distinguish between metallic silver and ionic silver which is also contained within the membrane throughout the experiment.

A check on the precision of the experiments is given in summing up the estimates for disposition of the silver oxide originally on Side 1, i.e., adding the amounts corresponding to radioactivity in Side 1, Side 2 and membrane at termination of an experiment. The original 45 ml. of saturated solution on Side 1 contained 2.57 milligrams of silver oxide, so the deviation from 2.57 of the values in the "sum" column are a measure of experimental error.

Inspection of Table I shows that there are essentially three different types of membrane included.

Type (1): The B and C type membranes take up only very small amounts of silver but allow small amounts of silver to diffuse through. The rate of diffusion is so slow that less than 1% of the silver in a cell with five wraps of C3 would be lost to self-discharge in a year. (See calculation in Appendix I of Final Report, Contract NAS-5-3467.) These cells have not short-circuited in the Burgess tests.

Type (2): Cellophane, E4 and PVAlc's, on the other hand take up considerable amounts of silver oxide, allowing relatively small amounts to pass through. These materials all contain polymers with readily oxidizable hydroxy groups, namely cellulose, hydroxyethyl cellulose and polyvinyl alcohol respectively. In the Burgess tests cells with both cellophane and E4 terminated by short circuit. Although cells with PVAlc 79 continued for 42 cycles without short circuit in the Burgess tests, subsequent tests at Crane (to be reported by NASF/GSFC) show that cells with PVAlc 79 did commence shorting at cycle 37. There seems, therefore, to be a definite correlation between high silver pickup and tendency to short-circuit.

Type (3): The S-type film, to be discussed further below, was unique in that it picked up only small amounts of silver oxide and also allowed it to pass through at only a very small rate.

In Figures 2 through 7, experimental diffusion data are plotted showing the change with time of the counts per minute per 0.05 ml. aliquot of cell solutions. The top curves show the loss of radioactivity in the isotope-labelled Side 1 of the cell. The bottom curves show the gain of radioactivity on the opposite Side 2.

In the case of Type 2 membranes, the loss of radioactivity on Side 1 is at first more rapid than the gain on Side 2, because there is initial removal of silver on the membrane. Eventually the loss and gain curves tend to have reciprocal slopes which can be taken as a measure of the true rate of diffusion of silver through the membranes. In this second stage further removal on the membrane has either stopped or is extremely slow. In view of the experimental errors discussed above, the last estimate of the true diffusion rate is provided by the slope of this second stage of the top curve.

In Type 2 membranes, the loss of radioactivity on Side 1 is much more rapid than the gain on Side 2 throughout the duration of each experiment, because silver oxide is continually being removed by the membrane and not permitted to pass.

In Type 3 membrane, copolymer S, the rates of change in radioactivity are slow on both sides of the cell.

Silver oxide pickup is graphically illustrated in Figure 8.

Figure 2 - Diffusion of Silver Through Separator Membranes (442-71)

B3 30% PuA in Methyl Cellulose

PUDO Cellophane

Compartment charged with Ag 110

Compartment Opposite

B3

Cellophane

B3

Cellophane

Radioactive Counts per .05 ml. sample

500

400

300

200

100

20

40

60

80

100

120

140

160

Time in hours

-10-
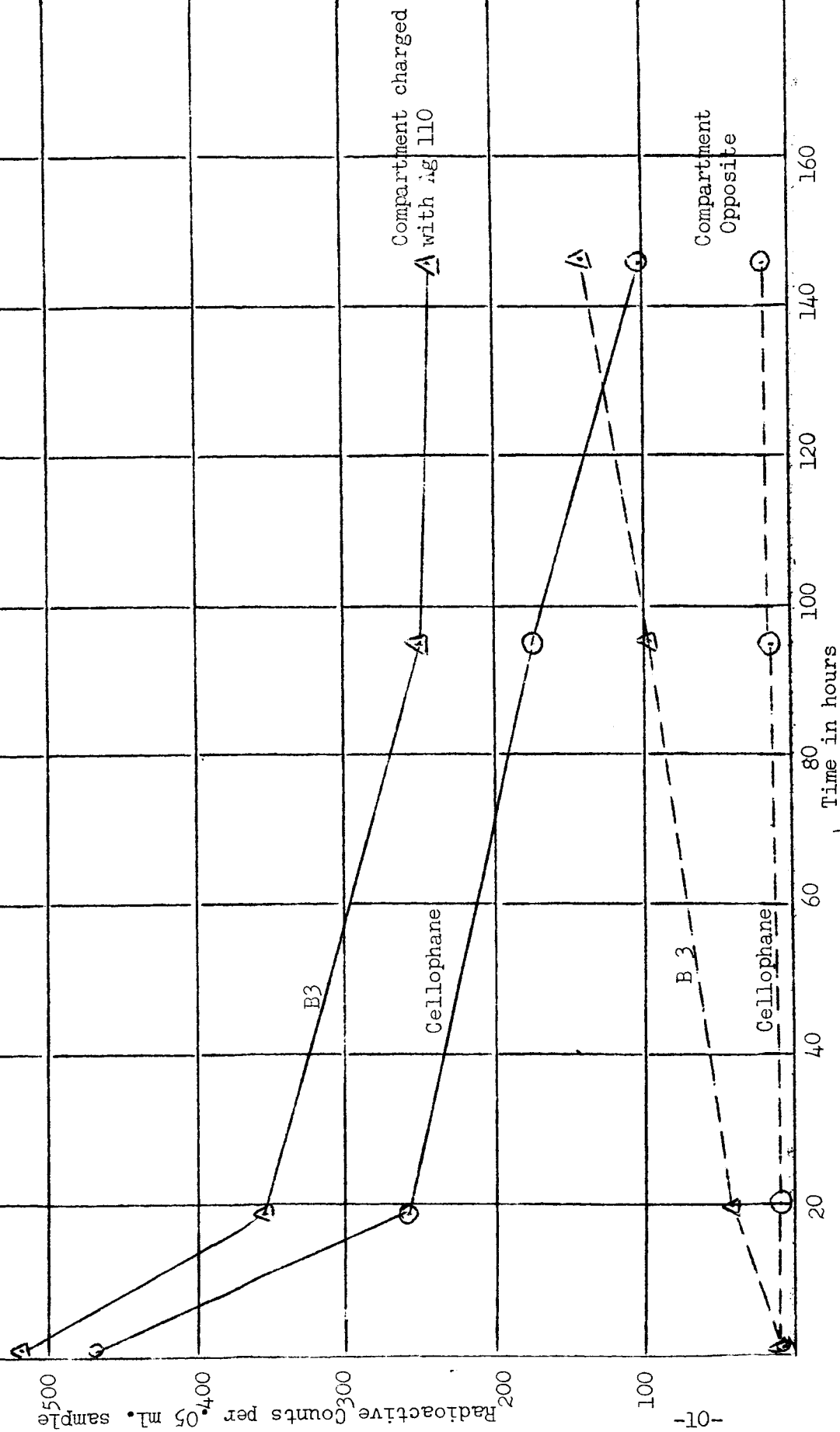
Figure 3: — Diffusion of Silver Through Separator Membranes (442-65)

E4, 35% Hydroxyethyl Cellulose in Methyl Cellulose △ ——
"PVAlc 79", Plasticized Polyvinyl Alcohol ⊙ ——

E4

PVAlc 79

Compartment Charged with Ag110

Compartment Opposite

Radioactive Counts per .05 ml. sample

500 400 300 200 100

20   40   60   80   100
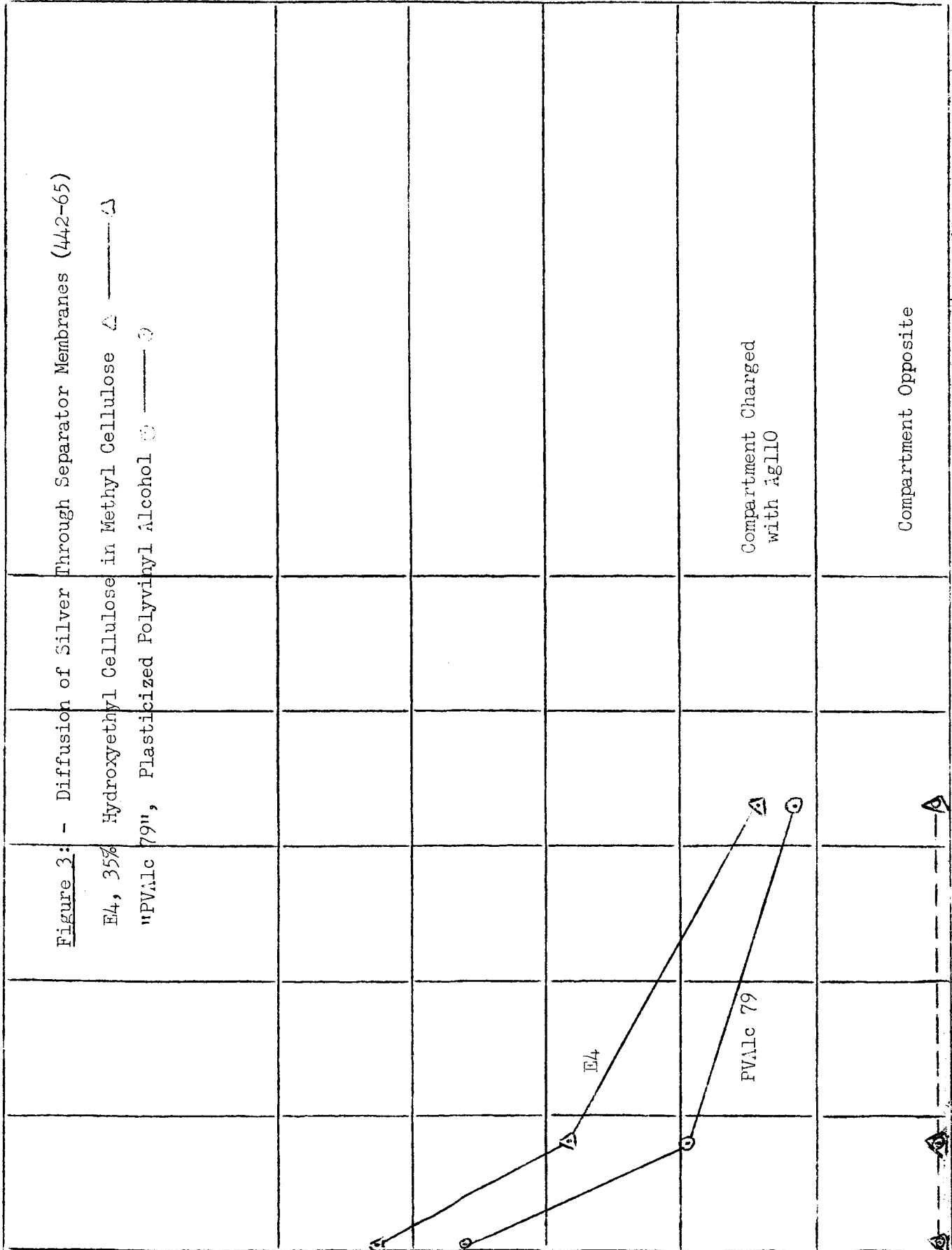
Time in Hours

Figure 4 — Diffusion of Silver Through Separator Membranes (442-52)

C1, 10% PVM/MA in Methyl Cellulose △——△

C3, 30% PVM/MA in Methyl Cellulose ○——○

Radioactive Counts per .05 ml. Sample

Time in hours

○ Compartment Charged with Ag110

○ Compartment Opposite

-12-

Figure 5 — Diffusion of Silver Through Separator Membranes (442-63)

S Film   (445-10)   ○
Polyvinyl Alcohol (374-61)   △ ———— △

S Film

PVAlc

Compartment charged
with Ag 110

Compartment Opposite

Time in Hours

Radioactive Counts per .05 ml.

-13-
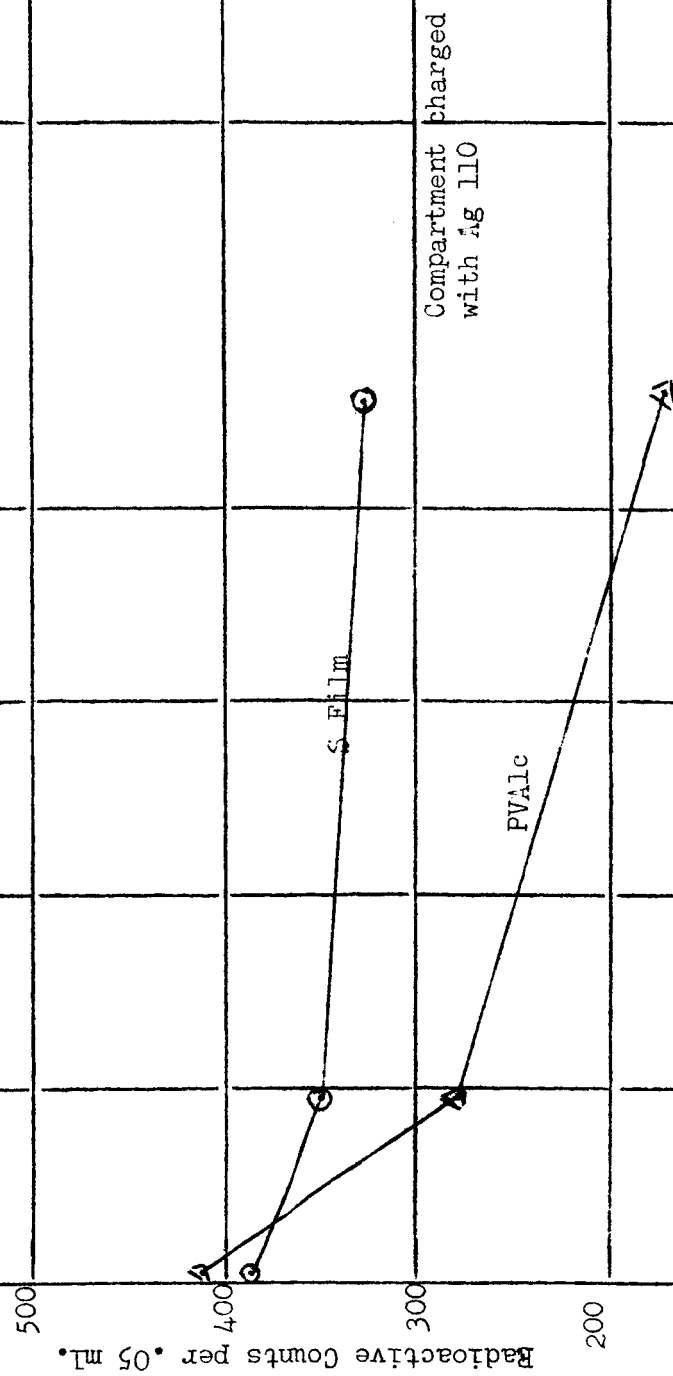
Figure 6 - Diffusion of Silver Through Separator Membranes (442-79)

B 3 30% PM in Methyl Cellulose ⊙ ——

C 3 30% PVM/MA in Methyl Cellulose △ ——

Compartment Charged with Ag 110

Compartment Opposite

Time in Hours

Radioactive Counts per .05 ml. sample

500 400 300 200 100

-14-
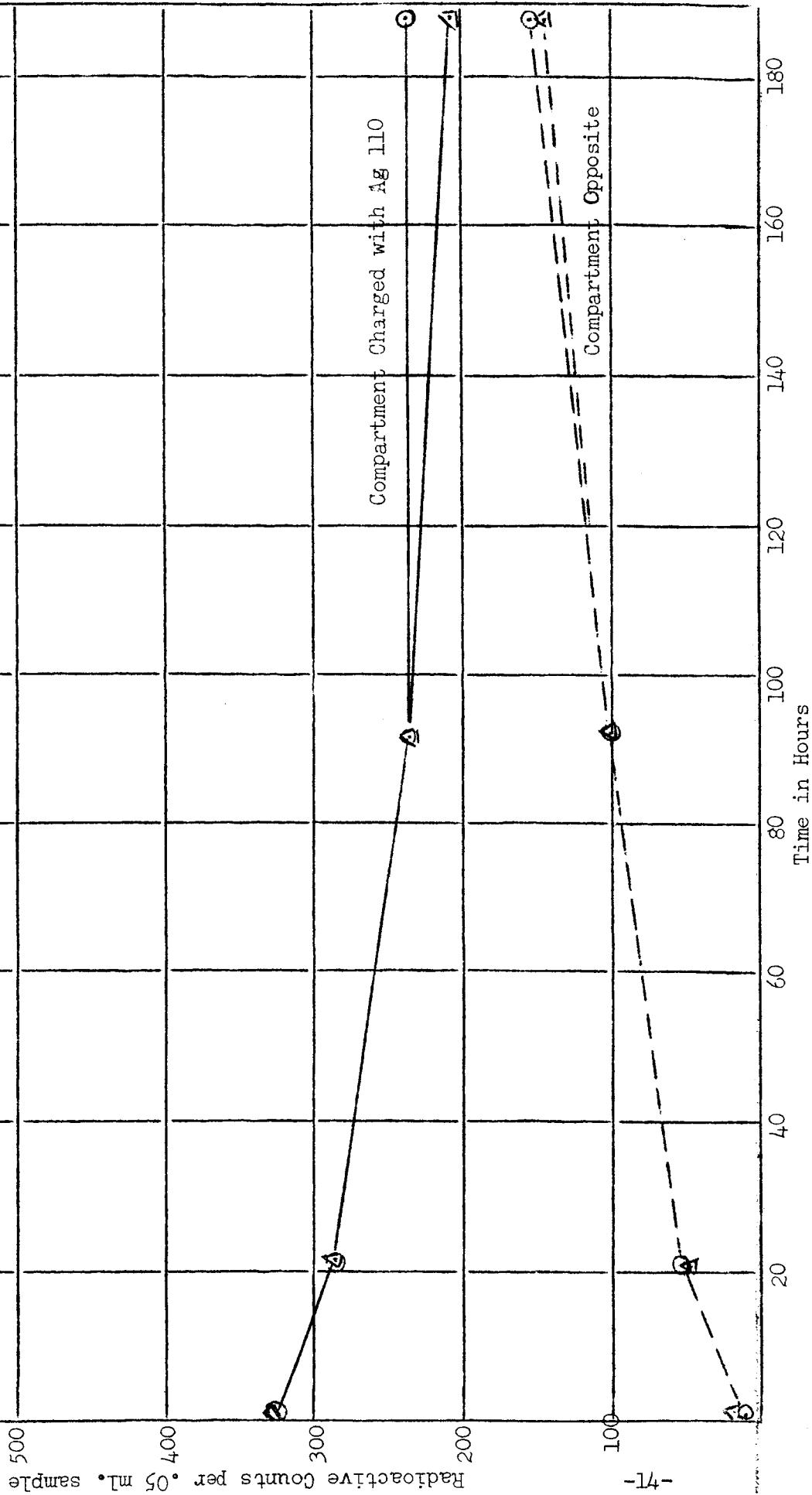
Figure 7 - Diffusion of Silver Through Separator Membranes (442-85)

C2 20% PVM/MA in Methyl Cellulose

S Film (445-26)

Compartment Charged with Ag 110

Compartment Opposite

C2

S Film

C2

S Film

Radioactive Count/.05 ml. sample

500
400
300
200
100

Time in Hours

20 40 60 80 100 120 140 160 180

-15-
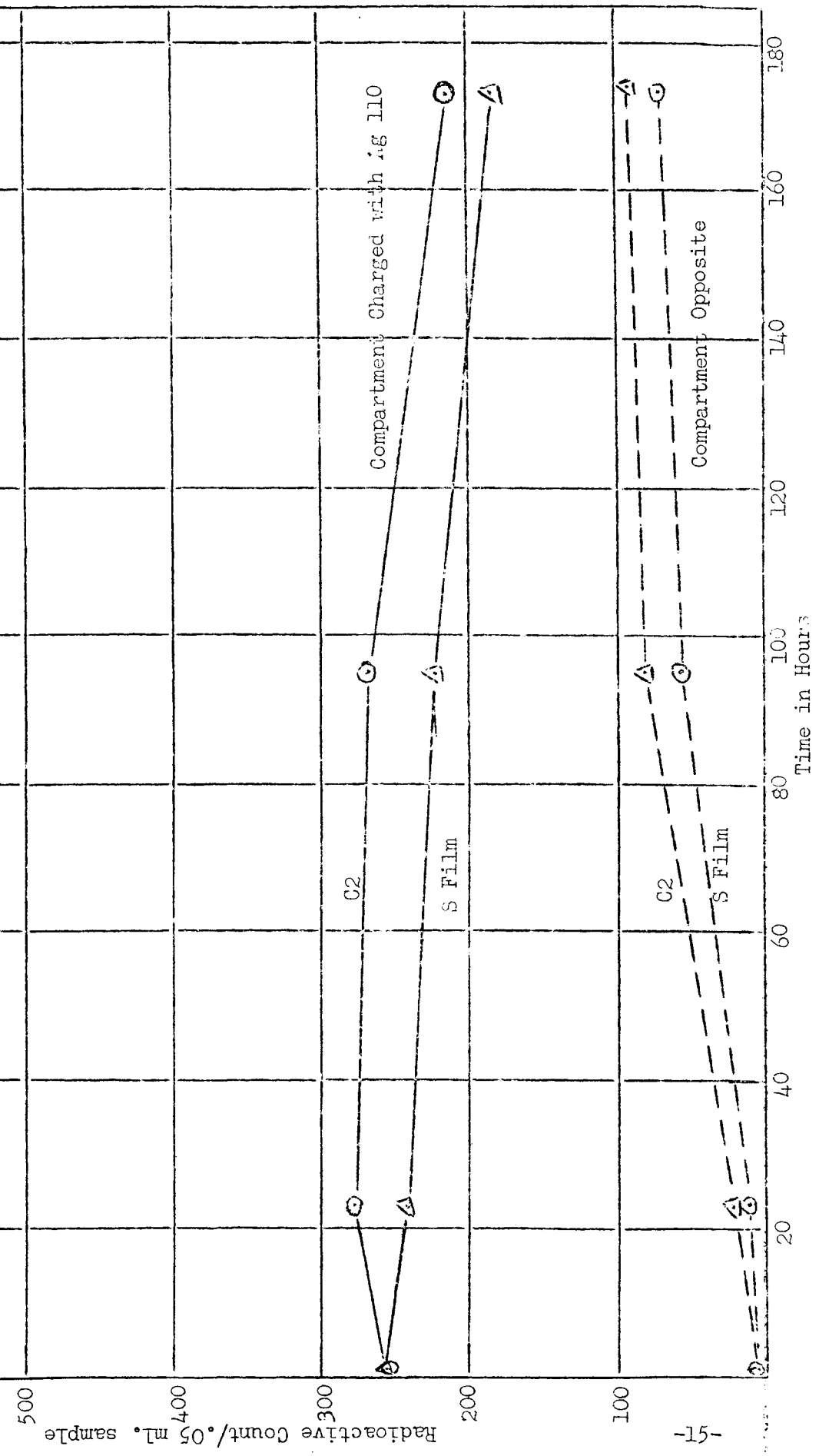
Figure 8 – Radioactive Silver Pickup by Membranes During Diffusion Experiments

X "PVAlc 79"

X PVAlc

X E4

X PUDO

C 3, ◯
B 3, ⊡

S, E4, "PVAlc 79", PVAlc, C1, C2, PUDO   x   (single points)

C3

C1

C2
X

S

B3

B3

HOURS

Radioactive Count x 10^5

3.0

2.0

0

20   40   60   80   100   120   140   160   180

-16-
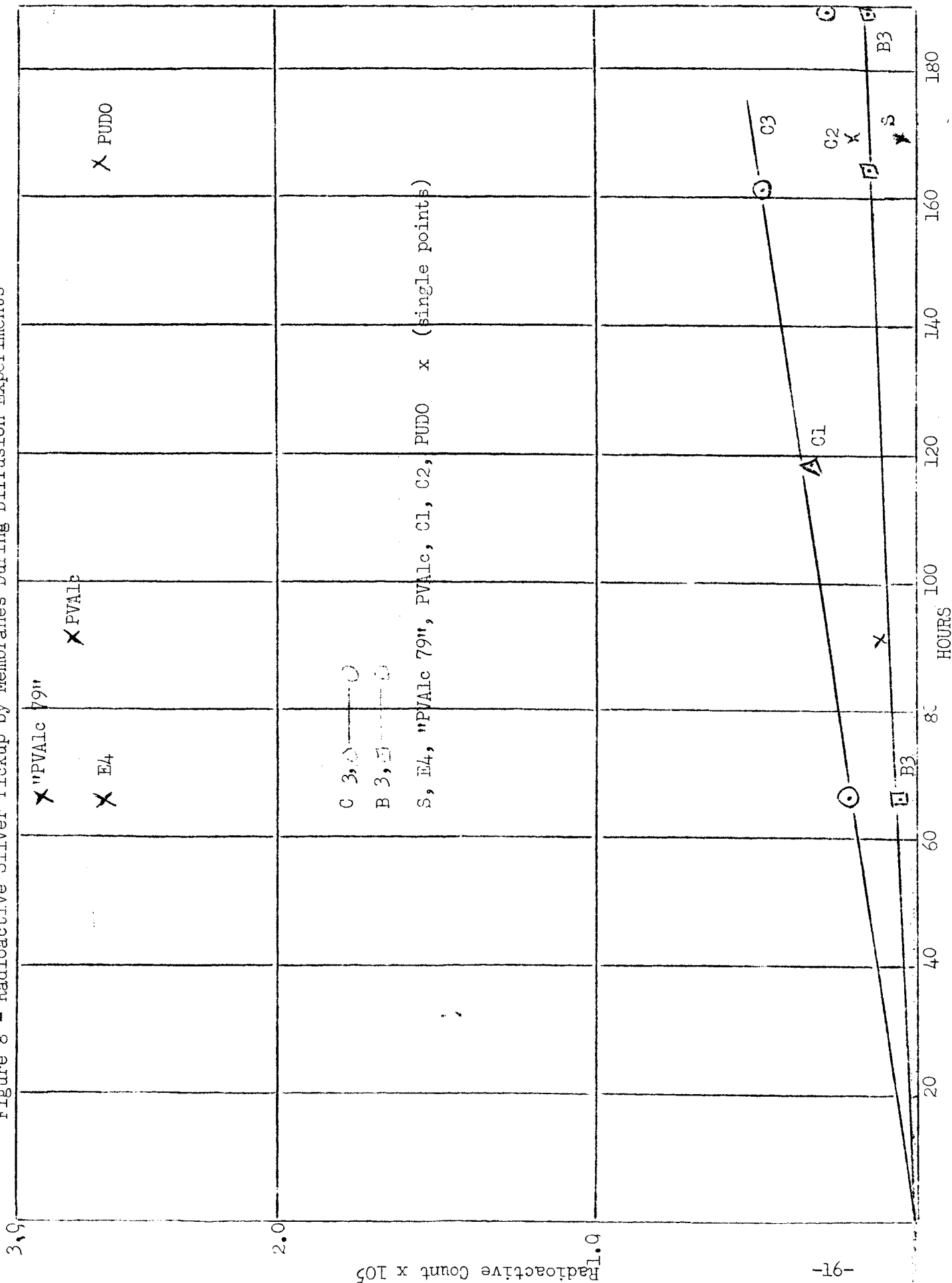
SECTION B - SYNTHESIS OF ACRYLIC COPOLYMERS

Acrylic polymers offer the advantage of high resistance to silver oxidation. Work has been started with the objective of attaining within a single molecule the required balance of high and lower polarity. Toward this end, monomers of high polarity are copolymerized with monomers of lower polarity. By varying the monomer ratio and studying the effect on membrane swelling and electrolytic conductivity, it is hoped to arrive at an optimum ratio. A complicating factor is that flexibility of the copolymer must also be in the desirable range.

Preliminary experiments were made copolymerizing acrylic or methacrylic acid as the highly polar monomer with methacrylic esters of various chain length. Typical examples are given in Table II. The polymers were too brittle.

An alternative method of preparing acrylic acid copolymers is to synthesize first a copolymer of methyl acrylate with a methacrylate ester, then hydrolyze. It was demonstrated that under conditions which hydrolyze the methyl acrylate moieties to acrylic acid, methacrylic esters or their polymers are not hydrolyzed. Table III summarizes several polymerizations with butyl methacrylate. After polymerization in methyl ethyl ketone, this solvent was replaced by isopropanol, and excess KOH was added as saponification catalyst. The hydrolyzed polymer was precipitated into excess hydrochloric acid. After filtration, washing and drying, the acid form of the copolymer was dissolved in dioxane, or other appropriate solvent for casting film. Although most of the films were too brittle to make useful separators by themselves, they were coated on 1.5 mil Webril non-woven Dynel cloth. These supported films were swollen in 30% KOH and their conductivity measured. Three of the copolymers of Table III had resistances comparable with unsupported C3 films. Solubility behavior also indicated that the right order of polarity balance had been achieved. These polymers were soluble in 2% KOH but insoluble in 30% KOH. Their brittleness is at least partially attributable to their low molecular weight which is also indicated by the low viscosities of their casting solutions. This work will be continued using more concentrated polymerization solutions in solvents such as benzene, conditions under which molecular weight is likely to be increased.

TABLE II

ACRYLIC POLYMERS

Experiment No. 407-	81	83	56	58	68	76
Molar Composition						
Ethyl methacrylate	–	–	.75	–	–	–
Butyl methacrylate	1.00	–	–	.70	.67	.30
2-Ethylhexyl methacrylate	–	1.00	–	–	–	–
Methacrylic acid	–	–	.25	.30	–	–
Acrylic acid	–	–	–	–	.33	.70
Solvent *	MEK	MEK	MIBK	MIBK	MEK	MEK
Temp. °C.	80	80	115	116	80	80
Time in hours	15	7	2.5	3.5	22.5	2.8
Conversion (%)	100	100	78	.78	83	83
Film character	brittle	liquid	v. brittle	v. brittle	v. brittle	v. brittle
Solubility (1 = insoluble)						
Water	1	1	1	1	1	1
30% KOH	1	1	1	1	1	1
2% KOH	1	1	1	–	1	sol. hot

* MEK = methyl ethyl ketone

MIBK = methyl isobutyl ketone

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TABLE III

METHACRYLATE–ACRYLATE COPOLYMERS

Expt. No:	407-78	407-88	407-90	436-41
Molar Composition				
Methyl acrylate	.70	.50	.40	.30
Butyl methacrylate	.30	.50	.60	.70
Solvent	MEK	MEK	MEK	MEK
Temperature – ° C.	80	80	80	80
Time – hours	23	7	13	7
Conversion – %	100	100	100	100
Physical State – before hydrolysis	visc.liq.	visc.liq.	visc.liq.	visc.liq.
after hydrolysis	solid	solid	solid	solid
Film description	v.brittle	v.brittle	v.brittle	v.brittle
Solubility in water	dispersed	insol.	insol.	insol.
in 30% KOH	insol.	insol.	insol.	insol.
in 2% KOH	sol.	sol.	sol.	insol.
Acid content meq/gram Found	6.52	2.89	2.83	1.64
Limit (a)	6.70	4.38	3.35	2.48
Electrical Resistance – ohms – in 30% KOH (b)	0.1	0.0	0.0	6.4

(a) "Limit" calculation was based on the assumption that the acrylate ester moiety of the formulation would be completely saponified and the methacrylate ester moiety not attacked.

(b) Supported on 1.5 mil non-woven Dynel cloth. Controls on polyvinyl alcohol and methyl cellulose gave 2.3 ohms and 10.4 ohms respectively. for an exposed diameter of .20 inches of film at equilibrium with the electrolyte. Measurements to the nearest 0.5 ohms.

Exploratory copolymerizations of other monomer systems are summarized in Table IV. The most promising of these were the four-component polymer 446-22.

TABLE IV

RESISTANCE AND FLEXIBILITY OF SELECTED COPOLYMERS

| Polymer | Type | | Film | | Resistance * | |
			Thick-ness (mils)	Flexibility	ohms in 30% KOH	Film in 30% KOH
446-8	MVK-MMA	70/100	1	Brittle	1,550	Brittle
446-10	MMA-MA	50/100	4.9	"	1,940	"
446-11	MMA-MA	100/50	2.0	"	215,000	"
446-12	PVA-MVK-MMA	50/100/50	1.5	Flexible	25	"
446-14Pl	MVK-HPMA	25/100	–	Brittle	–	Gel
446-21	Sty-MA-AN-FA	50/25/10/15	1.0	"	2,550	Brittle
446-22	MMA-IP-AN-AA	40/30/10/20	1.0	Flexible	198	Flexible
446-24	Sty-IP	50/50	1.3	Brittle	20,466	Brittle

Abbrev.:

AA	–	Acrylic acid
AN	–	Acrylonitrile
FA	–	Fumaric acid
HPMA	–	Hydroxypropyl methacrylate
IP	–	Isoprene
MA	–	Methylacrylate
MMA	–	Methyl methacrylate
MVK	–	Methyl vinyl ketone
PVA	–	Polyvinyl alcohol

Notes: * For an exposed diameter of .20 inches of film at equilibrium with the electrolyte. Measurement to the nearest 0.5 ohm.

SECTION C - "S-TYPE" MEMBRANES

An "S-type" copolymer, developed under another Borden project was cast in film form and found to show conductivity of the same order as the highly polar membranes developed under the previous contract. This was remarkable because the chemical structure was relatively non-polar and did not correspond to the observed conductivity. The membrane also showed an anomalously low degree of swelling in electrolyte. The behavior indicated a semi-permeable physical structure. A quantity of film was prepared for the construction of cells at Burgess. Resistance in the cells was found to be higher than anticipated from resistance measurements in our equipment and performance was unsatisfactory due to high internal resistance of the cell.

Permeability of the S-film (lot 445-19) to oxygen in the Dow cell was about 14 times greater than C3 films. It should be noted, however, that the test was made on films not swollen in KOH.

Further work in this area is warranted because of the unique properties of the film, low swelling, excellent flexibility, chemical resistance to silver oxide oxidation (see Section A) and excellent thermal stability. Attempts should be made to increase the conductance of this type of material without impairing its other properties.

SECTION D - ETHYLENE COPOLYMERS WITH POLAR GROUPS

Zetafin (Dow Chemical Co.) is a copolymer of ethylene and ethyl acrylate. Hydrolysis of the ester moiety could conceivably yield a conductive membrane. This was attempted by both alkaline and acid hydrolysis, without success.

A research quantity of a copolymer of ethylene and acrylic acid, designated 442-50B, was obtained from an outside source. The product, found by analysis to contain about 7 mol percent acrylic acid as the sodium salt, was sufficiently soluble in water to permit casting from ten percent solution after centrifugation to remove a small amount of suspended matter. The film was very brittle when dry but showed a low resistance in 30% KOH, about 0.3 ohms. Plasticization with 5% and 10% triethylene glycol gave weak but quite flexible films at the expense of greater electrical resistance, 7 and 10 ohms respectively. Resistance in 45% KOH, which augments measurable differences amongst films, showed a resistance of 80 ohms on the film containing 5% plasticizer as compared to an average resistance of 11 ohms for C3 films in our equipment.

Judged by fluidity of the solutions, the molecular weight of the product is relatively low. These polymers are of primary interest as potentially resistant to high temperatures.

SECTION E — UNUSUAL CELLULOSE DERIVATIVES

A number of less common cellulose derivatives were evaluated as potential membranes. Solubility and electrolytic resistance are given in Table V.

Of the new cellulosics of this group, 442-121-1, a low degree of substitution methyl cellulose, is of chief theoretical interest, showing far lower resistance than the usual commercial type methyl cellulose of high degree of substitution (421-86 of Table V.). Resistance in 45% KOH was of the same low order as given by cellulose, polyvinyl alcohol and, in the methyl-cellulose-polyacid combinations, C5 or B5 formulations. The rather high viscosity of aqueous solutions of this derivative introduces a practical difficulty in preparation of solutions and casting of films, necessitating the use of 2% solution instead of 10% as in the case of Methocel 15.

Ethulose, a new commercial product showed to advantage over Methocel 15 in conductivity and is under further study.

TABLE V

Miscellaneous Cellulose Derivatives – Solubility and Electrical Resistance

Film Prepn.	Description *		Solubility			Resistance**, ohms		
			H_2O	30% KOH	40% KOH	30% KOH	40% KOH	45% KOH
407-51	Klucel Type L	(E)	sol	insol	insol	3,151	5,201	–
407-49	CMHEC L	(A)	sol	sol	insol	too soft to test		–
407-50	CMHEC 37L	(B)	sol	sol	insol	too soft to test		–
436-25	EHEC 75H	(C)	swells(D)	insol	insol	2,383	87,000	–
421-86	MC 15 1.7 d.s.	(F)	sol	insol	insol	21	–	230
442-121-1	Methocel AS2 0.9 d.s.	(G)	(G)	insol?	insol	0	0	0.4
445-146	Ethulose	(H)	sol	insol	insol	0	–	20
485-122	CMC 4A	(I)	sol	sol	insol	sol	–	too soft

Notes: (A) Carboxymethyl hydroxyethyl cellulose d.s. 0.4 carboxymethyl, 0.3 hydroxyethyl (Hercules)
(B) Same, 0.3 carboxymethyl, 0.7 hydroxyethyl (Hercules)
(C) Ethyl hydroxyethyl cellulose, d.s. not stated (Hercules)
(D) Insoluble 28° C., soluble 10° C.
(E) Klucel (Hercules), composition not divulged.
(F) "Regular" Methyl cellulose of high degree of subs. (Dow)
(G) Low degree of substitution methyl cellulose (sol. in dil. alkali)(Dow)
(H) Contains $-OC_2H_5$ and $-OCH_2CH_2OH$ in cellulose (Chemaster Corp.)
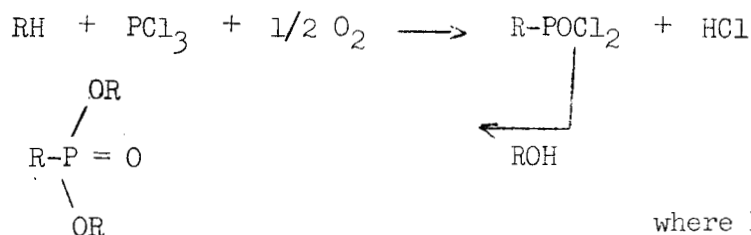(I) Low degree of substitution carboxymethyl cellulose (0.4 d.s.) Experimental sample, courtesy Hercules.

* d.s. is degree of substitution of glucose unit. Maximum possible is 3.0.

** For an exposed diameter of .20 inches of film at equilibrium with the electrolyte. Measurement to the nearest 0.5 ohm.

SECTION F - DERIVATIVES FROM CHLOROPHOSPHONATION
OF POLYOLEFINS

A reaction (6)(7)(8), which is quite general for suitable soluble polymers, consists of the action of phosphorus trichloride and oxygen as follows:

$$RH + PCl_3 + 1/2\ O_2 \longrightarrow R\text{-}POCl_2 + HCl$$

$$
\begin{array}{c}
\text{OR} \\
/ \\
R\text{-}P = O \qquad\qquad\qquad ROH \\
\backslash \\
\text{OR}
\end{array}
$$

where R may be H

The products would be expected to show good resistance to hot potassium hydroxide solutions. An exploratory investigation was made, using the apparatus pictured in Figure 9. This consisted of an electrically heated reactor (250 ml. 3 necked S.T. Pyrex flask) equipped with a gas inlet below the surface of the solution, thermometer in the liquid, stirring propeller, water cooled reflux condenser, surmounted by a dry ice-reflux condenser. During the period of heat-up and solution of the polyolefin in PCl_3 a slow stream of nitrogen was used as a purge. When the solution was complete and the desired reaction temperature attained nitrogen was replaced by metered oxygen, using a calibrated orifice flow meter from a constricted section of 8 mm. glass tubing and a differential manometer. The gases emerging from the dry ice condenser were led by Tygon tubing into two glass scrubbers in series to pick up HCl of the reaction. Titration as a measure of reaction progress proved to be unreliable because of PCl_3 in the emergent gas.

At the conclusion of each reaction the product was precipitated into highly cooled water or water-ethanol as detailed in notes of Table VI, conditions depending on aliquot testing for optimum precipitated form. The precipitated product was filtered at low temperature, washed with ice water and vacuum dried at low temperatures to minimize fusion of particles.

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(6) J. Appl. Poly. Sci. V, 157-62   E. C. Leonard et al
(7) U. S. Patent 3,008,939 (1961)   E. C. Leonard et al
(8) U. S. Patent 3,069,939 (1961)   E. C. Leonard et al
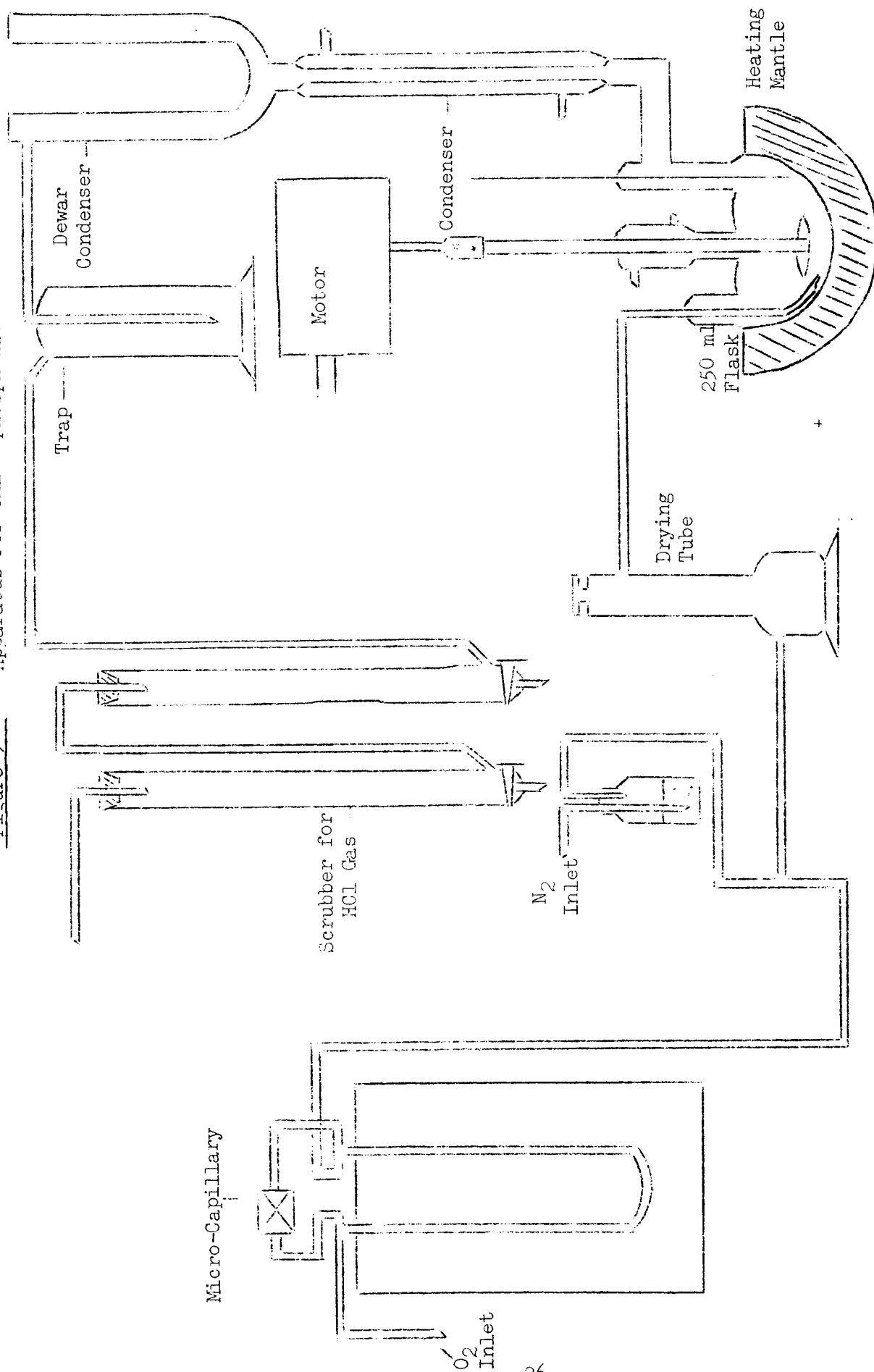
Figure 9 - Apparatus For Chlorophosphonation

Table VI. – Chlorophosphonation of Polyolefins, Followed by Hydrolysis

Prep. 436-	90 (EPR-404)	95 (EPR-404)	97 (EPR-404)	99 (ERP-404)	105 (EPR-404)	112 (Ultra-thene)	116 (EPR-404)	140 (EPR-404)
Polymer charged g.	5.0	5.0	5.0	5.0	5.0	5.0	5.0	10.0
PCl_3 ml.	130	130	130	130	130	130	130	300
O_2 Rate ml/min.	242	242	242	242	242	242	242	242
Reaction Time - hrs.	3.2	12.5	1.0	3.0	12.5	12.5	43	41
Temp. °C.	60-65°	60-65°	69-71°	70-73°	70-80°	70-76°	70-83°	69-79°
How Worked Up	(A)	(A)	(C)	(D)	(E)	(E)	(E)	(E)
Product Description	light tan	dark brown	almost white	white	white	white	dark brown	v.brown
Phosphorus %	–	–	–	.95	.84	–	7.11	9.3
Resistance** 30% KOH	–	–	–	1×10^5	1×10^5	–	4.6	*
Solubility Hot Xylene	sol	insol	sol	insol	swells	insol	insol	insol
Hot Dioxane	insol	insol	insol	insol	insol	insol	insol	insol
Molding	infus-ible	molded, porous	molded, rubbery	molded porous	molded	infus-ible	molded	molded

Notes: (A) Distd. off solvent. Reduced product in Waring Blendor in EtOH. Washed. Poor physical condition.

(C) Precipitated total prep. into ice and water. Reduced in Waring Blendor, washed.

(D) Precipitated total prep. into ice 50%, alcohol 50% + dry ice, washed. Good physical condition.

(E) Ditto. Pptn. in a Waring Blendor. Excellent physical condition.

* Polymer after soaking in 45% KOH was too swollen to handle. The polymer dissolved in 30% KOH.

EPR-404 = Ethylene propylene copolymer (Enjay)

Ultrathene – Ethylene copolymer with vinyl acetate (U.S.I.)

Preparations 436-101 and 436-103, not tabulated, were run according to conditions of 436-99. Products were white, infusible, insoluble. Starting material polyethylene Eastman 812A, 813A.

** For an exposed diameter of .20 inches of film at equilibrium with with the electrolyte. Measurement to the nearest 0.5 ohm.

The experiments are summarized in Table VI. As was anticipated a fairly high degree of phosphonation was required to produce polymers in the conductive range. This required rather long reaction times as noted. None of the products was sufficiently soluble to permit casting from solution, membranes being molded in a Carver Press. The highly phosphonated membranes were fairly flexible and dark brown in color. Preparation 436-116 was close to the required polarity for resistance and solubility. The attempted duplicate preparation, 436-140, was of higher phosphorus content, and was soluble in 30% KOH, and too soft in 45% KOH to afford a resistance measurement. The reason for failure to duplicate is not known.

It would appear that this reaction could be widely applied (9), subject to limitations in PCl_3 solubility. A sample of polyisobutyl rubber (Vistanex) proved to be soluble in hot PCl_3. A polypropylene polymer, Profax 6511J was totally insoluble.

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(9) J. Am. Chem. Soc. 70, 3880, Clayton et al